

## Hyperfine Structure in the Band Spectrum of the Mercury Hydride HgH

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The structure of the spectrum of the mercury hydride has been reinvestigated with a more powerful experimental arrangement. In 1931 a complex structure due to different isotopes of mercury was discovered (Part I) and a closer study with improved apparatus led in 1935 to the establishment of a new band spectroscopic effect of the so-called nuclear isotope shift (Part II), the correlation of which with the corresponding atomic effect was explained by Bohr. Certain differences in structure between lines belonging to different branches seemed to be detectable, and these differences were subjected in this paper (Part III) to a careful study. In the bands of the system  ${}^2\Pi_1 \rightarrow {}^2\Sigma$  a new (fifth) component was found on the short wave-length side for  $P$  and  $R$  band lines (Fig. 1). This component is gradually merging with the fourth for higher rotational energies. In the  $Q$  lines a corresponding component is overlapped with the fourth for lower rotational energies and causes for higher rotational energies a deviation of the measured position of the fourth component toward too small separations. Careful measurements of separation reveal that the fifth component in  $P$  and  $R$  lines should be correlated to the mercury isotope 199 (Fig. 2). Since the intensity of this component is

equal only to 9 percent of the total intensity of the group of components, the fifth component does not represent the whole contribution of 16.45 percent of the isotope 199. It is concluded therefore that the lines emitted by the molecules containing the isotope 199 must be split at least into two components. Thus a first proof of the existence of a hyperfine structure in band spectra is obtained. The approximate structures of groups of components corresponding to the odd isotopes 199 and 201 are obtained by subtracting the intensities corresponding to even isotopes from the intensity curves found by measuring the intensity distribution for the whole group of components (Fig. 3, a, b and c). No satisfactory explanation of the structures obtained could be found. The results of the measurements of the separation of components corresponding to even isotopes deviate from the expected ones (normal rotational isotope effect) and the deviation (difference of 27 percent in slope) cannot be explained by any known cause. An additional strong anomaly of a different kind is found for higher rotational energies in the bands of the system  ${}^2\Sigma^+ \rightarrow {}^2\Sigma$  (Fig. 4).

### INTRODUCTION

A NUMBER of years ago the author<sup>1</sup> found a complex structure in the band spectrum of the mercury hydride molecule. Already in 1918 Nagaoka<sup>2</sup> and in 1921 Gehrcke and Glaser<sup>3</sup> performed experiments designed to detect a structure of band lines in the same spectrum, a structure which would be analogous to the long-known, but not yet explained at that time, complex structure of the atomic spectrum of mercury. Their failure to observe the complex structure was probably caused chiefly by the inadequacy of their light sources for this purpose (broad lines). The structures found by the author<sup>1</sup> seemed to deviate from the structures expected for a normal rotational and vibrational isotope effect of different isotopes of mercury. Subsequent investigations<sup>4</sup> carried out with a more adequate apparatus and an improved technique led to the establishment of a new effect in band spectra, the so-called nuclear isotope shift. Nuclear isotope shifts were found later by the author also in the spectra of HgD,<sup>5</sup> HgH<sup>+</sup> and HgD<sup>+</sup>,<sup>6</sup> and finally in ZnH.<sup>7</sup> The correlation of this effect with the well-known isotope shift in the atomic spectrum of mercury was explained by Bohr.<sup>4,5</sup>

The study of such narrow structures requires the crossing of a high resolving interference apparatus with

a large prism spectrograph. Only band spectra of hydrides and deuterides were investigated until now, since they have sufficiently wide spacings between band lines. Moreover the existence of the nuclear isotope shift could be proved only for molecules containing the even isotopes of the metals. The structure of all lines found in HgH and HgD differs from the structure expected for a simple overlapping of the normal isotope effect with the nuclear shift, showing an anomalous behavior of the lines emitted by molecules containing odd isotopes of mercury. A similar effect of an apparent absence of lines corresponding to the odd isotopes of cadmium has been observed by Svensson<sup>8</sup> in the cadmium hydride spectrum. A tentative explanation of this behavior put forward by the author<sup>4,5</sup> was based on the assumption of a presence of a hyperfine structure causing a splitting of the lines in question into several weaker components. This explanation found a certain support in the results of the work on the spectra of HgH<sup>+</sup> and HgD<sup>+</sup>.<sup>6</sup> In this latter spectrum, which is of the type  ${}^1\Sigma \rightarrow {}^1\Sigma$ , no hyperfine structure splitting is expected. In agreement with this it was found that the lines corresponding to the odd isotopes seems not to reveal any anomalous behavior.

Since at the time no clear proof of the existence of a hyperfine structure in any band spectrum has been given,<sup>9</sup> the clarification of the origin of the deviations

<sup>1</sup> S. Mrozowski, *Zeits. f. Physik* **72**, 776 (1931). Subsequently will be designated as Part I.

<sup>2</sup> H. Nagaoka, *Sci. Pap. Inst. Phys. and Chem. Research (Tokyo)* **1**, 1 (1918).

<sup>3</sup> E. Gehrcke and L. C. Glaser, *Ann. d. Physik* **65**, 605 (1921).

<sup>4</sup> S. Mrozowski, *Zeits. f. Physik* **95**, 524 (1935). Part II.

<sup>5</sup> S. Mrozowski, *Zeits. f. Physik* **99**, 236 (1936).

<sup>6</sup> S. Mrozowski, *Phys. Rev.* **58**, 332 (1940).

<sup>7</sup> S. Mrozowski, *Phys. Rev.* **58**, 597 (1940).

<sup>8</sup> E. Svensson, *Nature* **131**, 28 (1933).

<sup>9</sup> A small but distinct broadening of the first few lines in branches was observed by Hulthén and Heimer (*Nature* **129**, 56 (1932)) for the  ${}^1\Sigma \rightarrow {}^1\Pi$ -bands of bismuth hydride BiH. This broadening was tentatively explained as an unresolved hyperfine structure splitting. The author made a few photographs of these bands and also of the AlH bands with the big Chicago grating, but was unable to find any structure in view of the considerable

of finer details in the complex structure of the spectra HgH and HgD seemed of considerable importance. Already in Part II certain peculiarities in the structure of lines and differences in intensity distribution between lines belonging to *Q* branches on one side, and to *P* and *R* branches on the other were noted. They are especially well visible in the (0, 0) band of the  ${}^2\Pi_3 \rightarrow {}^2\Sigma$ -system ( $\lambda 4017$ ). The closer examination of these anomalies was the starting point of this investigation. This paper constitutes therefore the Part III of the author's work on the complex structure of the lines in the spectrum of HgH. The photographs of the spectrum were made in Poland in the summer of 1939 at the Institute of Theoretical Physics of the University of Warsaw, the microphotometer recordings were obtained a few years later at the Department of Physics of the University of Chicago. The results of this investigation gave the first convincing proof of the existence of hyperfine structure in band spectra. They were briefly reported at a meeting of the Am. Phys. Society several years ago.<sup>10</sup> More recently hyperfine structures due to electric quadrupole moments of the nuclei were found by others in pure rotational spectra of a number of molecules (microwave region). Since in this work a splitting of levels is found for the isotope Hg<sub>199</sub> which has a nuclear spin  $\frac{1}{2}$  (no quadrupole moment) the hyperfine structure here reported is undoubtedly due to the interaction of the electrons with the magnetic moments of the nuclei. In other words the effect here reported is an exact counterpart of the hyperfine structure in atomic spectra.

#### EXPERIMENTAL

The experimental arrangement was the following: an all water-cooled mercury arc of a special design (Part II) was run in an atmosphere of hydrogen at low current densities (0.7–0.9 amp. per cm<sup>2</sup>). The discharge was observed in an end-on arrangement. As a high resolving instrument a heavily aluminized (Hochheim's alloy) Fabry-Perot etalon with different plate separations was used. The interference pattern was projected by an excellent achromatic lens on the slit of a 1.5 meter large interchangeable spectrograph of Hilger. This time a high speed glass optics was available for this spectrograph and the bands in the region  $\lambda 3600$ – $\lambda 4400$  could be obtained with a considerably higher dispersion than before, the dispersion being for instance for the band  $\lambda 4017$  around 5A/mm in comparison to 13 A/mm used in Part II. The improvement in comparison to Part II was however much greater than the ratio of these numbers would indicate, since a Fabry-Perot etalon is giving smaller separations between consecutive orders than does a Lummer-Gehrcke plate and consequently considerably smaller widths of the spectrographic slit could be used. Thus many lines could

be easily observed in regions which were inaccessible before on account of overlappings. Especially the investigation of the region of the band  $\lambda 4017$ , which is reproduced in Fig. 1 and which constitutes the immediate long wave-length extension of the part reproduced in Fig. 2, Part II, was of great importance.

With such an arrangement the exposure time did not exceed 10 minutes. For such short exposures no special precautions to keep a constant pressure and temperature had to be observed. Photographs were made using also a hollow cathode discharge tube instead of the mercury arc. Construction details of the hollow cathode tube were given in a previous paper.<sup>6</sup> In view of the lower temperature of the gas in the discharge tube, sharper components are obtained. However, the branches are much less extended, therefore such plates were used only for measurements of separations in the immediate neighborhood of the band origins. The intensity of the band spectrum is much lower and considerably longer exposures had to be used (1 hour or more).

#### RESULTS

##### Separation of Components

A photograph obtained with the mercury arc and a Fabry-Perot etalon of 11.2 mm plate separation is reproduced in Fig. 1. Characteristic differences can be detected in the structure of different lines. Comparing for instance the two neighboring lines  $Q_{120}$  and  $R_{12}$ , marked by dots on Fig. 1, we see that  $Q_{120}$  has two strong central components, a weaker one on the side of shorter wave-lengths and a very weak one on the side of long wave-lengths. In  $R_{12}$  we find two strongest and the weakest components, but the short wave-length component is split into two components both of them being weaker than the corresponding single component of  $Q_{120}$ , but both stronger than the weakest component of  $R_{12}$  and  $Q_{120}$ . This difference is typical for the *P* and *R* lines on one hand and *Q* lines on the other, as it can be seen by inspection of Fig. 1. The separation of the short wave-length doublet in *P* and *R* decreases in the band toward the shorter wave-length's, so that beyond the mercury atomic line marked in Fig. 1, no splitting is observed any more. The two components merge into a single one and the structure of the *R* lines becomes similar to the *Q* lines. On the other hand, for very high rotational quantum numbers the distance of the short wave-length component from the central one increases less rapidly for the *Q* lines. The component becomes wide and loses its sharpness, especially on the side of the longer wave-lengths (toward the strong central doublet). Approximately the same relations are found in the (0, 1) band  $\lambda 4219$ ; since however the isotope effect separations are smaller the *P* and *R* lines even for high rotations still reveal a fifth component. The *Q* lines show only 4 components without any decrease in sharpness.

width of the lines. It appears that such a study should be carried out not with a common discharge tube, but with a hollow cathode tube at liquid air temperature.

<sup>10</sup> S. Mrozowski, Phys. Rev. 63, 63 (1943).

The state of affairs for the band  $\lambda 4017$  is best seen from Fig. 2, where the results of the measurements of separations of components for a great number of lines are given. The distances of components were measured on several plates for different Fabry-Perot plate separations with a traveling microscope and the separations determined by a non-linear interpolation (taking the variation of the distances of consecutive orders into consideration). For the two central components (Nos. 2 and 3) a very good straight line dependence is found; a little less consistent results are obtained for the weakest component (No. 1). For the short wave-length component (No. 4) the splitting for *R* and *P* lines into two components (Nos. 4 and 5) at longer wave-lengths and the deviation of No. 4 at higher frequencies toward smaller separations for the *Q* lines are well represented.

If the correlation to the different even isotopes of mercury given in Part II is true, the components Nos. 1-4 correspond to isotopes of mercury 204, 202, 200 and 198. It is then evident from Fig. 2 that the fifth component having an intermediate slope of the line in Fig. 2 (between 200 and 198) should belong to the isotope 199. However, the intensity of this component is slightly smaller than that of the fourth, and therefore does not represent the total contribution of the isotope 199 to the pattern (see below the results of measurements of intensities). Another component belonging to 199 should be present and is probably overlapped with the component No. 3. For the *Q* lines and for longer wave-lengths the component No. 5 is probably almost exactly overlapped with No. 4 producing a relatively higher apparent intensity of the component No. 4. The gradual separation of the two for higher frequencies produces the relative decrease of the measured separation of components Nos. 3 and 4, and the broadening of the component No. 4.

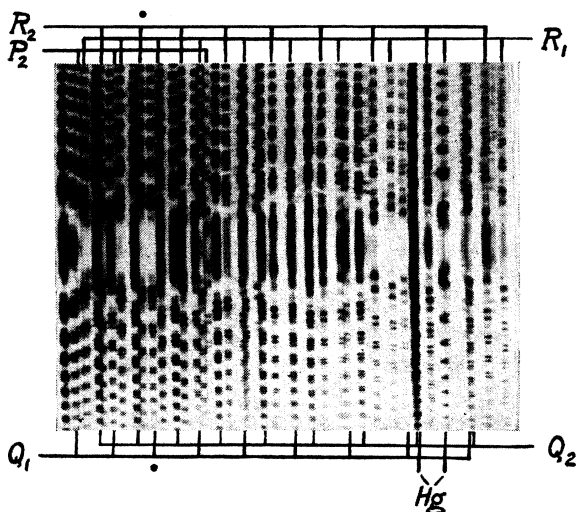


FIG. 1. Photograph of a part of the (0,0) band at  $\lambda 4017$  of the mercury hydride system  ${}^2\Pi_1 \rightarrow {}^2\Sigma$  made with a Fabry-Perot etalon and a large glass spectrograph. *Q* lines reveal four, *P* and *R* lines five components.

The separation of components for the even isotopes of mercury at the position of the band origin (zero line) is given by the very small normal vibrational isotope effect of  $0.008 \text{ cm}^{-1}$  and the much greater nuclear isotope shift of about  $0.062 \text{ cm}^{-1}$ . The last value is obtained from the average of the distances 1-2, 2-3 and 3-4; it is a little smaller than the value reported in Part II (for the reason see below). The slope of the lines in Fig. 2 is given by the rotational isotope effect relative to the isotope 201 taken as the horizontal line of reference. For two mercury isotopes differing in mass by one unit  $1-\rho$  is equal to  $\delta = 1.21 \times 10^{-5}$ , the expected slopes of the lines No. 3 (and No. 2) and No. 4 (No. 1) are  $2.\delta = 2.42 \times 10^{-5}$  and  $6.\delta = 7.3 \times 10^{-5}$ . Instead of this we find  $3.1 \times 10^{-5}$  and  $9.3 \times 10^{-5}$ , that is values greater by more than 27 percent. This deviation was already noticed in Part II and was explained by Bohr as an increase of the nuclear isotope shift caused by the increase of the separation of the proton from the nucleus of the mercury atom at higher rotations. However, the measurements were not as accurate as the present ones and it was believed at that time that the deviations occur only at higher rotational quantum numbers. Therefore the extrapolation to the zero band line was executed assuming only a normal rotational isotope effect in the neighborhood of the band origin, and the value for the nuclear isotope shift found  $0.0665 \text{ cm}^{-1}$  was higher than the value obtained in this paper. With the new measurements for HgH and the new way of determination of the separations at the band origin the difference in the linear dependence of the nuclear isotope shift from the oscillational energy found previously for the spectra HgH and HgD (see Fig. 4 of reference 5) turns out to be non-existent, both lines being given by the same equation  $\Delta\nu_{\text{n.ose.sh.}} = 0.0554 + 1.03 \times 10^{-5} \times \nu_{\text{ose.}}$

Stenvinkel<sup>11</sup> suggested a different explanation for the deviations from the normal rotational isotope effect. He pointed out that instead of the simplified formula for the rotational isotope effect used by the author, namely  $\Delta\nu_{\text{rot}} = (1-\rho^2) \cdot \nu_{\text{rot}}$ , the more general formula should be applied, namely

$$\Delta\nu_{\text{rot}} = (1-\rho^2) \cdot K - (1-\rho^3) \cdot L - (1-\rho^4) \cdot M$$

where

$$K = B_e' J'(J'+1) - B_e'' J''(J''+1),$$

$$L = \alpha_e'(v'+\frac{1}{2}) J'(J'+1) - \alpha_e''(v''+\frac{1}{2}) J''(J''+1),$$

and

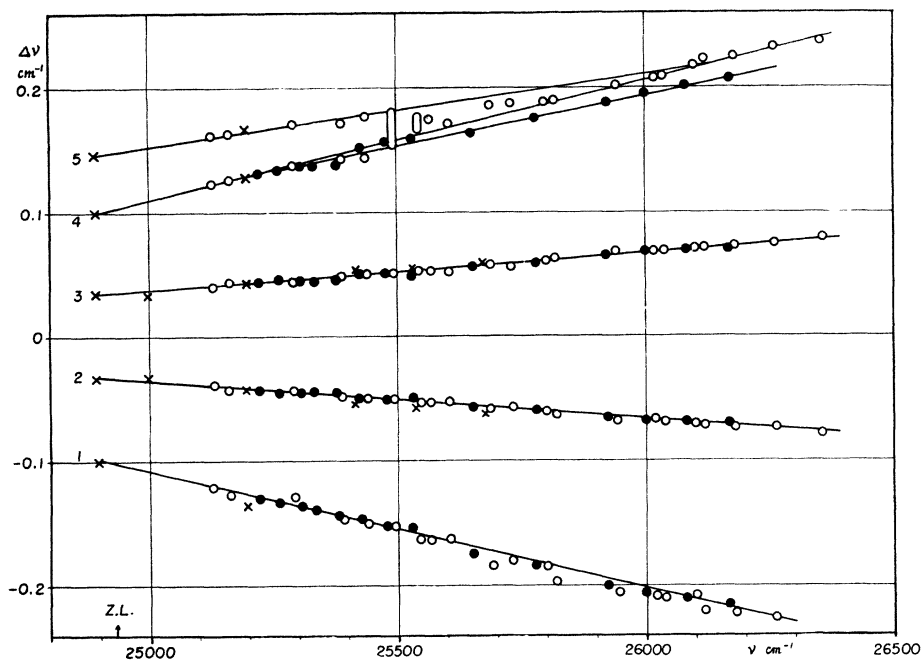
$$M = D' J'^2 (J'+1)^2 - D'' J''^2 (J''+1)^2.$$

A deviation from the simplified formula in the same direction as the observed one will be obtained. The deviation from the simplified formula can be easily calculated using the values of the constants for the HgH spectrum reported by Rydberg<sup>12</sup> and by Fujioka and

<sup>11</sup> G. Stenvinkel, "Das bandenspektrum des zinkhydrides," dissertation, Stockholm (1936).

<sup>12</sup> R. Rydberg, Zeits. f. Physik 73, 74 (1931).

FIG. 2. Separations of components measured in the band  $\lambda 4017$ . Open circles—lines belonging to *R* branches, filled in circles—*Q* branch lines, crosses—*P* branch lines.



Tanaka.<sup>13</sup> Since  $\nu_{\text{rot}} = K - L - M$  and for small  $\delta$ 's  $1 - \rho^n = n \cdot \delta$ , we get  $\nu_{\text{rot}} = 2\delta \cdot \nu_{\text{rot}} - \delta \cdot L - 2\delta \cdot M = 2\delta(\nu_{\text{rot}} - \frac{1}{2}L - M)$ . Substituting  $\alpha' = 0.25$ ,  $\alpha'' = 0.312$ ,  $D' = 2.9 \times 10^{-4}$ ,  $D'' = 3.8 \times 10^{-4}$ , we find for  $J'$  and  $J''$  around 30 a formula  $\Delta\nu_{\text{rot}} = 2\delta(\nu_{\text{rot}} + 100)$ . The correction of  $100 \text{ cm}^{-1}$  can give only an explanation of a small part, in fact not more than one-fourth of the observed deviation for the *Q* and *R* band lines. The small extra deviation for the *P* lines (crosses around  $\nu = 25500 \text{ cm}^{-1}$ ) toward higher separations can be explained very well by Stenvinkel's correction. However the linear dependence of the main deviation from the rotational frequency  $\nu_{\text{rot}}$  and the absence of a greater deviation for *P* lines presents a difficulty for any kind of explanation including the one suggested by Bohr (Part II). It was thought at first that maybe too small separations are obtained toward the band edge due to an attraction of components for smaller separations, but this seems hardly probable, since the results were checked with Fabry-Perot etalons with several different plate separations.

It can also be seen from a comparison of the mercury hydride and mercury deuteride spectra, that the deviation cannot be caused by any correction terms from the formula for the normal rotational isotope effect. For a given  $\nu_{\text{rot}}$  (high quantum numbers  $J$ ) the deviation given by the member  $M$  in the formula should constitute the same percentage of the normal separation in both spectra, that is the deviation should be double for the mercury deuteride. For the member  $L$  the contribution of which is smaller than of the former one in these spectra, the deviation should be  $\sqrt{2}$  times bigger than

for the hydride spectrum. In the spectrum of the mercury deuteride<sup>5</sup> however the absolute deviation is smaller than in the hydride spectrum and constitutes only 10 percent of the total rotational separation. The linear dependence of the separation from  $\nu_{\text{rot}}$  is easily noticeable on Fig. 2 of the paper on the mercury deuteride spectrum.<sup>5</sup>

### Relative intensities

In order to obtain more information about the hyperfine structure in the spectrum of mercury hydride the intensity distribution in the complex structure for many lines in the band  $\lambda 4017$  was investigated. Alternately with the Fabry-Perot photographs of the mercury hydride spectrum direct photographs of a pure mercury arc spectrum from another source were made on the same plate. The slit of the spectrograph was illuminated by the light of this source avoiding the interference apparatus by inserting a prism in front of the slit. A sharp image of a platinum step filter was focused on the slit and by an appropriate lens arrangement a uniform illumination of the whole image was obtained. The densities of the interference patterns and of the comparison intensity marks were determined with a recording microphotometer (Moll-Type *A*). The transmission of the steps in the filter was measured for different wave-lengths using a monochromator and a photo-cell. The microphotometer recordings were evaluated and the intensity distribution in a group of components was determined applying a procedure described by the author in a paper on isotope shifts in the atomic spectrum of boron.<sup>14</sup> Corrections for the

<sup>13</sup> Y. Fujioka and Y. Tanaka, Sci. Pap. Inst. Phys. and Chem. Research (Tokyo) 34, 713 (1938).

<sup>14</sup> S. Mrozowski, Zeits. f. Physik 112, 223 (1939).

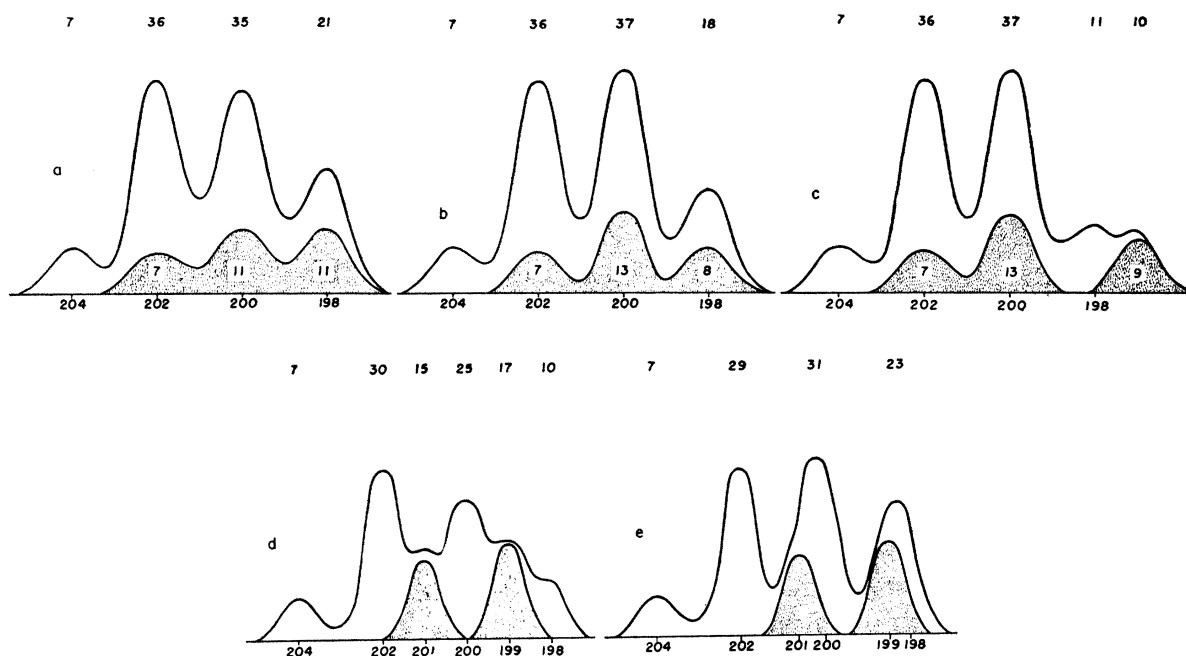


FIG. 3. Intensity distribution in a group of components for lines of the band  $\lambda 4017$ : (a)  $Q_2$  lines around  $25500\text{ cm}^{-1}$ , (b)  $R_1$  lines around  $25800\text{ cm}^{-1}$ , (c)  $R_2$  lines around  $25300\text{ cm}^{-1}$ , (d) predicted structure in absence of hyperfine structure and for an even distribution of isotopes of mercury, for lines around  $25700\text{ cm}^{-1}$ , (e) predicted structure in absence of hyperfine structure but for an asymmetrical position of odd isotopes (like in the atomic spectrum of mercury), for lines around  $25700\text{ cm}^{-1}$ .

scattered light were subtracted. The final curves obtained are far from being as accurate as in the case of the spectrum of boron. A less sensitive microphotometer was used this time and a wider slit in the microphotometer had to be applied in view of the small width of the spectrographic slit. A considerable amount of extra broadening of components was thus introduced in the pattern. Less importance therefore should be attached to the exact shape of the lines and the considerations should rather be limited to a discussion of the total intensity of a component (that is to the area enclosed by the curves).

The results obtained are presented in Fig. 3, graphs a, b, and c. Graph a gives a typical intensity distribution for a  $Q_2$  branch line, the curve was obtained as an average from several  $Q_2$  lines in the neighborhood of  $\nu = 25500\text{ cm}^{-1}$ . Graph b is for  $R_1$  lines around  $\nu = 25800\text{ cm}^{-1}$ , where the fourth and fifth component are already merged together into one, and graph c is for  $R_2$  lines around  $\nu = 25300\text{ cm}^{-1}$  (both are averages over several lines). As can be seen from these graphs, the difference noticed in Part II concerning a higher intensity of the component No. 3 (isotope 200) in  $R$  lines than in  $Q$  lines appears to be real. The curves were drawn assuming the same total intensity for the first component in all three cases. It was expected that this is the only component to be likely free from overlappings and its intensity should be proportional to the concentration of the isotope 204. For this end the curves were approximately decomposed into single curves corresponding to different components and their areas determined

by use of a planimeter. The assumption turned out to be well supported by the experiment, since the area of the first component was found to be in all cases equal or a little bigger than 7 percent of the total area of the group (see Table I). To the total intensity of the remaining components (Nos. 2-5) all other mercury isotopes are therefore contributing. By subtracting the intensities of the even isotopes 202, 200 and 204 from the pattern the shaded areas were found, which approximately represent the distribution of intensities in the group of components emitted by the odd isotopes 201 and 199 of mercury. Since there are at least three components and only two emitting isotopes the existence of a hyperfine structure splitting in this band spectrum is thus definitely established. The shaded areas give only a very rough (smeared-out) picture of the structure of the spectrum corresponding to an overlapping of the pattern for two odd isotopes, since the presence of several closely spaced components overlapped with the strong lines of the even isotopes (202 and 200) could be only revealed by a very accurate study of the shape of the lines, which was made impossible in this case by the considerable width of the slit used in the microphotometer. The uncertainty in the intensities corresponding to the shaded components should not be bigger than  $\pm 2$ . The internal consistency of the results for different band lines was much higher, but since there are so many factors affecting the final values, the author thinks it better to refrain from claiming any higher accuracy.

In Fig. 3, two graphs d and e are added in order to

compare the structures obtained with structures predicted for the case of an absence of hyperfine structure splitting. Graph d gives the expected structure of a group for the case of an even distribution of isotopes (like in the normal isotope effect) and graph e represents the expected structure for lines around  $\nu=25700$   $\text{cm}^{-1}$  and for an overlapping of the normal effect with a nuclear isotope shift, assuming the nuclear isotope shift to be proportional to the shifts observed in the atomic spectrum of mercury (centers of gravity for isotopes 201 and 199 very near to the positions of isotopes 200 and 198). For higher rotations the components corresponding to odd isotopes would move away from the even isotopes 200 and 198 (normal rotational effect) and a structure approaching Fig. 3d would be observed (around  $\nu=26300$   $\text{cm}^{-1}$  6 components should be found). The numbers given on top of each graph are relative peak intensities. Although the last curve bears some similarity with curves a and b the difference in peak intensities is well outside of the limits of errors of the measurements.

As to the theoretical interpretation of the hyperfine structure patterns for the two odd isotopes it seems to present certain serious difficulties. Hulthén<sup>9</sup> pointed out that the coupling of the nuclear spin with the molecular axis should break down already at low rotational energies and for medium and high rotational quantum numbers  $J$  the nuclear spin should be coupled with the axis of rotation of the molecule. For the excited state  ${}^2\Pi$  a very small hyperfine separation is expected since the electronic orbital momenta and the electronic spins are coupled with the molecular axis and the interaction should at least partly average out for all except the lowest rotational energy states. In the ground state  ${}^2\Sigma$  both the electronic spin and nuclear spin are coupled with the axis of rotation and their interaction should cause an observable splitting, especially since the  $p\sigma$ -electron has an not negligible density of wave function in the neighborhood of the nucleus.<sup>5</sup> A total separation of the order  $0.1$   $\text{cm}^{-1}$ , which is considerably smaller than the separations in the hyperfine structure of the

TABLE I. Concentration of isotopes of mercury in percent.

Isotope	Concentration
204	6.85
202	29.3
201	13.7
200	23.8
199	16.45
198	9.9

atomic levels of mercury (for instance,  $0.7$   $\text{cm}^{-1}$  for  $6^3P_1$ ) seems to be of the right order of magnitude. For all branches a similar hyperfine structure is expected, which should be a partially overlapped doublet ( $I_{199}=\frac{1}{2}$ ) with an inverted quartet ( $I_{201}=\frac{3}{2}$ ) with separations approximately independent from the rotational energy. However, this is not in agreement with observations. To explain the difference in separation and in relative intensities of hyperfine structure components for different branches the existence of a measurable separation in the  ${}^2\Pi_1$ -state and the emission of components corresponding to transitions involving a change of the direction of the nuclear spin relative to the rotational axis has to be assumed. But then the similarity of the structures for  $P$  and  $R$  lines becomes difficult to explain. In conclusion the author finds himself unable to suggest any satisfactory interpretation of the results.

#### The ${}^2\Sigma^+ \rightarrow {}^2\Sigma$ -Bands

In connection with this work the system  ${}^2\Sigma^+ \rightarrow {}^2\Sigma$  of short wave-length bands was reinvestigated using a Fabry-Perot etalon and the quartz optics for the spectrograph. Results of measurements of the separations for the two strongest components are given in Fig. 4. The presence of the anomaly reported in Part II for the  $32700$   $\text{cm}^{-1}$  band is checked and a similar anomaly is found for the band  $33900$   $\text{cm}^{-1}$ . Toward longer wave-lengths (away from the band origin) the separations after reaching a minimum start increasing, instead of showing a steady decrease. Further the slope of the decrease in the neighborhood of the band origin is about 15 to 20 percent smaller than expected. The intensity distribution in the lines correspond to Fig. 3c with the

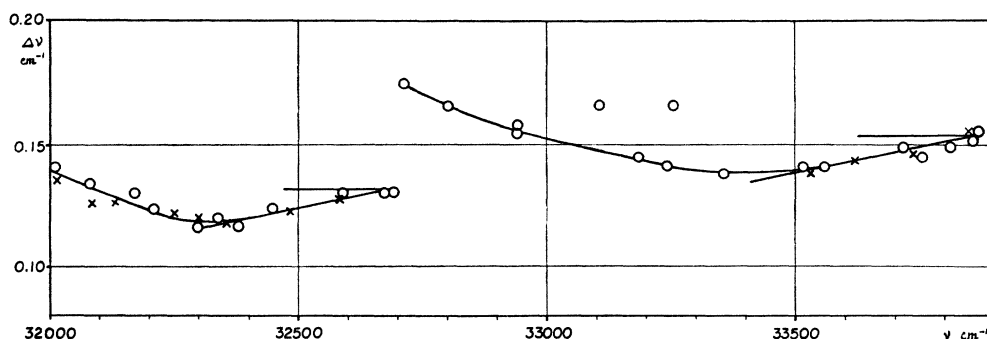


FIG. 4. Separation of the two strongest components in lines of the bands of the  ${}^2\Sigma^+ \rightarrow {}^2\Sigma$ -system of the mercury hydride. The anomalous increase of the separation in the long wave-length parts of each band is so strong as to overbalance the linear decrease caused by the normal rotational isotope effect. Circles—new measurements, crosses—previous results reported in Part II.

only difference that the fifth component (9 percent of total intensity) is in a considerably greater distance from the fourth component, approximately equal to the distance of the third and fourth components (200–198). All *P* and *R* lines reveal a similar structure.

This work was undertaken in the hope to clarify certain minor features of the structure of the lines in the spectrum of the mercury hydride, and to bring about the first proof of the existence of hyperfine structure in band spectra. The author believes that the second aim was achieved in a satisfactory manner. However, the general relations have not been clarified by this in-

vestigation. Just on the contrary, attempts to find an explanation of the hyperfine structure and of the deviations from the normal rotational isotope effect are meeting serious difficulties. It seems that a clarification of the problems brought forward can be expected from a thorough theoretical study of hyperfine structure and nuclear isotope shift effects in diatomic molecules.

*Note added in proof.*—The availability of concentrated samples of the isotope  $\text{Hg}_{199}$  has been recently announced [C. P. Keim, *Phys. Rev.* **76**, 1270 (1949)]. A corresponding study of the hyperfine structure of its hydride spectrum is in preparation at this laboratory.

## Some Aspects of Paramagnetic Relaxation

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This paper concerns the effect of interactions inside the spin system in giving a finite line width to the energy absorption lines in an oscillating magnetic field. The principal calculations are of absorption coefficients at low frequencies for copper salts. These absorption coefficients refer in most cases to the aperiodic line near zero frequency and not to the Larmor line. The first step is a discussion of the general procedure for reconstructing a shape function  $f(\nu)$  from its moments. The special case in which the zeroth, second, and fourth moments are known arises in the absence of a constant magnetic field, and at the Larmor frequency in a constant magnetic field perpendicular to the oscillating field. These cases are discussed and compared with experiment in Section III; extensive calculations have already been made by Van Vleck in the second case. The magnitude of the exchange coupling is the decisive factor, as pointed out by Gorter and Van

Vleck; and various methods of calculating this magnitude from experimental data are given. Low frequency absorption in a perpendicular field is discussed on the basis of a Gaussian approximation in Section IV, and the agreement with the experiments of Volger, Vrijer, and Gorter is good. In Section V it is shown that quantitative calculations only emphasize the discrepancy, pointed out by Broer, between theory and experiment for low frequency absorption in a parallel constant field. An explanation of the discrepancy is given in terms of the difficulty in resolving out the different lines in this case, due to the exchange broadening of the Larmor line, in contrast to the exchange narrowing of the Larmor line in a perpendicular field. In Section VI a calculation of the isolated susceptibility of a spin system is given for strong fields; it is found to be 0.80 of the thermodynamic or adiabatic susceptibility of Casimir and du Pré, even in the absence of exchange.

### I. INTRODUCTION

THIS paper is a condensation of the doctoral thesis submitted by the author at Harvard University, June, 1949. Its purpose is to discuss quantitative calculations on energy absorption by a paramagnetic salt in a magnetic field; these calculations being restricted to absorption in which the line breadth is due to interactions inside the spin system. The calculations of this paper are similar to those of Van Vleck<sup>1</sup> on the Larmor line in a perpendicular field; in the following paragraphs line shapes will be calculated for other lines of interest.

There are three principal cases which concern us; those in which the energy levels of the salt between which the absorption takes place are those which exist

A. in the absence of a constant magnetic field ( $H=0$ ),

B. in the presence of a field  $H=H_D$  perpendicular to the relatively weak field  $H_0 \exp(2\pi i\nu t)$  from which energy is absorbed,

C. in the presence of a field  $H=H_c$  parallel to the oscillating field  $H_0 \exp(2\pi i\nu t)$ .

<sup>1</sup> J. H. Van Vleck, *Phys. Rev.* **74**, 1168 (1948).

These three cases have been studied experimentally at relatively low frequencies by Gorter, Broer, and others at Leiden.<sup>2,3</sup> Cases A, B, and C are treated in Sections III, IV, and V, respectively. Remarks concerning the applicability of these methods to absorption at the Larmor frequency in a perpendicular field are made at the conclusion of Section III. Energy absorption at the Larmor frequency and at double the Larmor frequency in a parallel field is approached from the more familiar standpoint of the so-called isolated susceptibility of the spin system in Section VI. Absorption at high multiples of the Larmor frequency has not been investigated experimentally. Figure 1 summarizes the investigations made here and elsewhere on paramagnetic relaxation phenomena.

Broer<sup>4</sup> has shown that energy absorption due to spin-spin interaction is characterized completely by the

<sup>2</sup> L. J. F. Broer and J. Kemperman, *Physica* **13**, 465 (1947).

Volger, de Vrijer, and Gorter, *Physica* **13**, 62 (1947).

<sup>4</sup> L. J. F. Broer, thesis, Amsterdam, 1945.

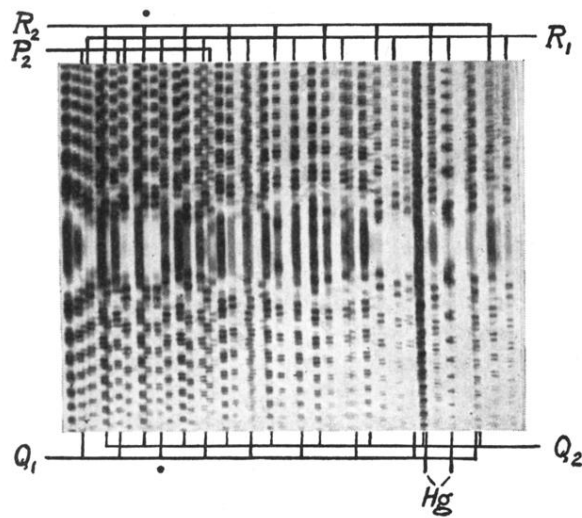


FIG. 1. Photograph of a part of the (0, 0) band at  $\lambda 4017$  of the mercury hydride system  ${}^2\Pi_1 \rightarrow {}^2\Sigma$  made with a Fabry-Perot etalon and a large glass spectrograph.  $Q$  lines reveal four,  $P$  and  $R$  lines five components.